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The Identification of Acids

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY

EDWARD LYONS

BALTIMORE, MARYLAND

June, 1917

EASTON, PA.:
ESCHENBACH PRINTING CO.
1917

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wool in a funnel with a short stem. The solution is cooled quickly and if the preparation has gone well the *p*-nitrobenzyl bromide separates in fine needles, very nearly white and melting at 99°.

If the reaction mixture has been heated above 130° or the reaction has gone wrong for some other reason, the bromide crystallizes in flakes and is difficult or impossible to purify by recrystallization. In this case the bromide can be purified by extracting it several times with ether which removes the impurities rapidly without dissolving much of the bromide. In Table I are given the results of about half the experiments that were made. The other half gave essentially the same results. The yield stated is for the purified product. In most cases the sealed tube was heated in a heavy copper tube which gave very uniform temperature.

It appears that 50 to 60% of the calculated amount may be obtained as the pure product. The best temperature is 125°.

TABLE I.

No.	<i>p</i> -Nitro- toluene. G.	Bro- mine. G.	Temp.	Time. Hours.	Yield, % of calcu- lated.	First m. p.	Final m. p.	Remarks.
1	10	11.6	110-2°	1	Bromine not used up.
2	10	11.6	110-1°	3	5.0	90°	90-96°	Product colored red.
3	20	23.2	115-6°	3.5	48.0	96°	99°	Crude product slightly red.
4	20	23.2	120-2°	2	55.5	99°	...	Crude product white.
5	70	80.6	120-5°	4	29.0	90°	99°	Temp. went to 135° for 20 min.
6	25	29.0	120-5°	2	54.0	98°	99°
7	30	34.8	125-7°	2.5	48.0	96°	99°	Looks flaky.
8	20	23.2	125-6°	2	36.5	96-8°	99-9.5°	Looks flaky.
9	22.5	25.0 ¹	126-9°	3.5	21.5	92°	99°	Ether purification required.
10	40	46.7	120-30°	2.5	60.0	99°	...	Crude product white.
11	20	25.0 ²	130-1°	2	32.0	85°	99°	Br ₂ not used up.
12	20	23.2	142-3°	2.5	48.0	97°	99°	Ether purification required.
13	20	23.2	148-50°	2	34.0	90°	99°	Ether purification required.

The temperature is doubtful in Experiment 10, since the heating was done in an ordinary bomb furnace and it was afterwards noted that temperature at ends was lower than in the center.

In Experiments 3, 5, 8, 10 and 13, the bromine was added in two portions.

Wachendorf prepared *p*-nitrobenzyl bromide by adding bromine to *p*-nitrotoluene at 180°. This has been repeated varying the conditions. The *p*-nitrotoluene was placed in a flask with an air condenser. It was heated in an oil bath the temperature of which is given in the table. The bromine was admitted through a tube which ended below the surface of the melted *p*-nitrotoluene and was added at the rate at which it seemed to react. This required about thirty minutes. The mixture was stirred

¹ Calculated 26.1 g.

² Calculated 23.2 g.

during the reaction. At the higher temperatures, the reaction is rapid during the addition of the first half of the bromine but slows down later. The product was extracted with portions of hot alcohol and ether as required. The crude product was dark colored but it was not difficult to obtain, the bromide melting at 99°. The results are given in the table below. There was no reaction at 100° and the *p*-nitrotoluene was recovered unchanged. Experiment 4 was carried out in the sunlight but no improvement was observed. Red phosphorus was added as a possible catalyst in Experiment 8. The reaction was violent but the yield was poor.

TABLE II.

No.	<i>p</i> -Nitrotoluene. G.	Bromine. G.	Temperature.	Yield. %.
1.....	10	11.6	100°	None
2.....	10	11.6	150°	10.5
3.....	10	11.6	180-5°	35
4.....	30	34.8	180-5°	30
5.....	10	11.6	180-5°	24
6.....	10	11.6	200-20°	5
7.....	20	30	180-5°	30
8.....	25	29	180-5°	..

The temperature 180°, used by Wachendorf, appears to be the best. By this method the yield is only about half that it is in the sealed tube but it has the advantage that it is carried on in an open vessel and requires less time. Since *p*-nitrobenzyl chloride is readily made by nitrating benzyl chloride, the nitration of benzyl bromide was tried. Benzyl bromide was made by dropping the calculated amount of bromine into toluene kept at 0° in the sunlight. During the reaction it was stirred rapidly by a mechanical stirrer. Benzyl chloride is readily nitrated by a mixture of 1 part fuming nitric acid and 2 parts of sulfuric. The same mixture seemed to nitrate benzyl bromide but a very small amount, only one or two per cent of the solid *p*-nitrobenzyl bromide, could be isolated from the product.

Since *p*-nitrobenzyl chloride can be readily obtained in large amount, its transformation into the bromide was studied. The best yield is obtained by boiling *p*-nitrobenzyl chloride in 95% alcohol with an excess of sodium bromide. A good yield is obtained but it is contaminated with unchanged chloride so that by the time it is purified up to m. p. 99° only about 25% is obtained.

Method of Work.

The method of work was the same as that previously described, with the exception that the salt was made in the reaction flask. A weighed amount of the acid and calculated amount of sodium carbonate with the

appropriate amount of water were put in the flask and then the alcohol and reagent were added. A slight excess of acid was always used, since it is desirable not to have an alkaline solution which would cause transformation into ethyl ester.

The various crops are designated 1st 1st and 1st 2nd, etc., meaning 1st crystallization 1st crop and 1st crystallization 2nd crop. The second crops were in most cases discarded, after weighing and getting the melting point since high purity rather than quantity was desired.

RESULTS.

p-Nitrobenzyl Esters of Aliphatic Acids. Monobasic Acids.

Monobromoacetic Acid.—The acid, 0.32 g., figured on 0.50 g. R, was neutralized with 0.10 g. NaOH (3 cc. standard solution). This, added to the reagent dissolved in 5 cc. 95% alcohol, gave a clear solution. This was boiled one hour. On rapid cooling to 0° the reaction mixture gave an emulsion. On standing overnight, white needles appeared. The 1st 1st was 0.07 g., m. 75–80°, crystallized from 33 cc. 12% alcohol gave 2nd 1st 0.04 g., m. 88–9°. Recrystallization from 2 cc. 50% alcohol gave 3rd 2nd, m. 88–9°. The ester seems to decompose at the melting point. The filtrates from the successive crystallizations gave nothing on dilution.

Benzilic (Diphenylhydroxyacetic) Acid.—The salt (from 0.52 g. acid + 0.12 g. sodium carbonate) in 2.5 cc. water was mixed with 0.50 g. R, dissolved in 5 cc. alcohol. The ester began to appear after 5 minutes' boiling. Thirty cc. 95% alcohol kept it in solution during the hour. Twenty cc. water were then added to saturation. The solution had to be cooled in ice to induce crystallization. The 1st 1st which was felt-like crystals weighed 0.55 g., m. 96°. A mixt m. p. with the reagent was 85°. Crystallization from 13 cc. alcohol gave 2nd 1st 0.42 g., m. 99–100°. Recrystallized from 15 cc. alcohol gave 3rd 1st 0.40 g., m. 99.5°. A mixture, half R and half ester, melted at 75°.

Leucin (α -Aminoisobutyl-acetic Acid).¹—This mixture was made of 0.5 g. of the reagent, the sodium salt (from 0.30 g. acid + 0.12 g. carbonate) and alcohol. Ten cc. 95% alcohol had to be added to dissolve the greenish emulsion formed on boiling. Precipitation of ester took place on standing overnight. The 1st 1st was 0.13 g., m. 198–9°. This crystallized from 25 cc. 50% alcohol gave (on standing—the ester does not precipitate at once) 2nd 1st 0.10 g., m. 191°. Recrystallization gave 3rd 1st 0.05 g., m. 184–6°, and this crystallized from 10 cc. 50% alcohol gave 4th 1st 0.03 g., m. 184–5°, with decomposition. The filtrates on dilution remained clear. This preparation was not satisfactory.

¹ This acid, the two amino acids that follow and α -aminobutyric acids were kindly furnished us by Dr. P. A. Levine to whom we wish to express our thanks.

Phenylalanin (β -Phenyl- α -aminopropionic Acid).—The sodium salt of this acid was made in an alcoholic solution since no action took place between the acid and carbonate in water. The mixture, 0.50 g. R, the salt (from 0.37 g. acid + 0.12 g. carbonate) and the usual amount of alcohol gave a greenish solution which on further boiling yielded white, flaky and very insoluble crystals. (Precipitation was not prevented by the addition of 55 cc. 95% alcohol.) The mixture was boiled three-quarters of an hour and filtered hot. The filtrate gave 1st 1st 0.32 g., m. 130° and 1st 2nd, 0.07 g., m. 130°. The insoluble was 0.25 g., m. 221–3°. This, on purification with alcohol, gave 0.23 g., m. 221–1.5° with decomposition. The 1st 1st gave a lower m. p. (117°) on crystallization from 63% alcohol and was discarded. This ester is also one of the most insoluble ones.

Alanin (α -Aminopropionic Acid).—The salt (from 0.20 g. acid + 0.12 sodium carbonate), 0.5 g. R, and 7.5 cc. 63% alcohol gave a greenish solution on boiling, with a precipitation of white plates. The solution on cooling was filtered. The filtrate could not be induced to crystallize. The insoluble ester was 0.07 g., m. 210–3°. Treatment with 10 cc. boiling 95% alcohol gave 0.05 g., m. 220–30°. A similar treatment gave 0.03 g., m. 228–30°. The ester begins to decompose (red vapors) at about 220°, then melts completely at 228–30°.

Levulinic Acid.—The salt was made by neutralizing 0.27 g. of the acid (figured on 0.50 g. R) with 0.10 g. NaOH (3 cc. standard). To this was added the R and 5 cc. 95% alcohol. Solution remained clear on boiling. Cooling, even in ice, gave only an emulsion. Long, silken needles 0.10 g., m. 58–60°, appeared overnight. An oil which had separated also solidified into a mass of flat crystals, 0.30 g., m. 60°. These, combined and crystallized from 13 cc. 34% alcohol, gave, on ice cooling, 2nd 1st, 0.32 g., m. 60.5°. Recrystallized as above gave 3rd 1st 0.30 g., m. 60.5–61°. Lyman and Reid reported failure with this acid.

Hydroxyisobutyric Acid.—The sodium salt was made by neutralization of 1.0 g. of the acid with concentrated sodium ethylate in absolute alcohol. To this was added 1.0 g. R, and 5 cc. water and the mixture boiled. The cooled solution remained clear. Five cc. water were added. Nice crystals appeared on standing a few minutes. The 1st 1st was 0.08 g., m. 80.5°. The 1st 2nd was 0.71 g., m. 80.5°. This being too close to the m. p. of the acid (79°), a mixt. m. p. was taken. It was 65°. Recrystallization of the two above from 5 cc. 95% alcohol gave 2nd 1st, 0.43 g., m. 80–5° and 2nd 2nd 80.5°.

α -Aminobutyric Acid.—The usual mixture of 0.5 g. R, the sodium salt (from 0.24 g. acid + 0.12 g. carbonate) and 15 cc. 63% alcohol gave a greenish cloudiness. Further boiling precipitated the ester (white crys-

tals). Forty cc. 95% alcohol did not hinder the precipitation. The solution was filtered hot. The insoluble was 0.10 g., m. 223°. The filtrate gave 1st 1st 0.10 g., m. 221°. Crystallization from 80 cc. 74% alcohol gave 2nd 1st 0.08 g., m. 222-3°, melting with decomposition.

Uric Acid.—A mixture of 0.5 g. R, 0.47 g. acid, 0.16 g. potassium carbonate and 15 cc. alcohol was boiled one and one-half hours. Thirty cc. 95% alcohol did not keep the ester in solution. The mixture was filtered hot. The filtrate gave 1st 1st, 0.08 g., which did not melt at 300°, and 1st 2nd, 0.20 g., m. 90°. The insoluble residue was 0.31 g. not melted at 300°. This was combined with 1st 1st and boiled with 60 cc. 80% alcohol. The filtrate gave 0.03 g., and insoluble was 0.22 g. not melted at 305°. This preparation was abandoned on account of its not melting at convenient temperature.

Pyromucic Acid.—To the sodium salt in water (0.26 g. acid + 0.10 g. carbonate) was added 0.50 g. R, dissolved in 5 cc. alcohol. The clear solution after boiling gave copious white crystals, 1st 1st 0.30 g., m. 131-2° and 1st 2nd 0.07 g., m. 104°. The m. p. 131-2° being close to that of the acid (132-4°), a mixt m. p. with the acid (m. p. 130°) was taken. It was 110° and 108-9° in a second trial. The above dissolved in 13 cc. 70% alcohol gave 2nd 1st 0.30 g., m. 133.5°. Recrystallized the 3rd 1st was 0.27 g., m. 133.5°. Repetition of this experiment gave identical results. The acid dissolved readily in sodium carbonate solution while the ester did not dissolve even on boiling.

Cyanouric Acid.—One of the hydrogens being more readily replaceable the acid was figured as monobasic. The 0.50 g. R was dissolved in 5 cc. 95% alcohol and added to the sodium salt (from 0.39 g. acid + 0.12 g. carbonate) in 2.5 cc. water. Sixty cc. 95% alcohol were required to keep the ester in solution. The 1st 1st was 0.18 g., m. 284°. Dissolved in 120 cc. 95% alcohol the 2nd 1st was 0.03 g., m. 284° and 2nd 2nd was 0.03 g., m. 284°.

Stearic Acid.—On heating a mixture of 0.50 g. R and sodium stearate (from 0.65 g. acid + 0.12 g. carbonate) in 7.5 cc. 63% alcohol, a jelly was precipitated. This went into solution on addition of 20 cc. alcohol. A nice lot of crystals precipitated on cooling (along with a jelly which was probably soap). The whole was boiled with water which dissolved the jelly, leaving the crystals, 0.12 g. not melted at 285°. This looked rather suspicious. Another experiment gave similar results. By boiling the jelly with water an insoluble residue was obtained which did not melt at 250°. The experiment was abandoned.

Palmitic Acid.—Here as in the case of stearic acid, the jelly was extracted with repeated washing with water and small portions of 95% alcohol. The 1st 1st, 0.40 g., m. 60-70°, yielded 2nd 1st 0.15 g., m. 51°.

Crystallization from 12 cc. 80% alcohol gave fine, white crystals 3rd 1st 0.12 g., m. 45°. Crystallized again the 4th 1st was 0.10 g., m. 42-42.5° and recrystallization from 10 cc. 76% alcohol the 5th 1st was 0.09 g., m. 42-42.5°.

Margaric Acid.—This acid was converted to the sodium salt by neutralizing with NaOH (0.50 g. acid + 0.07 g. base). Instead of the bromide *p*-nitrobenzylidide was used. An emulsion on cooling turned to mass of crystals overnight. The 1st 1st was 0.60 g., m. 45-51° and 1st 2nd 0.12 g., m. 45-100°. The 1st 1st dissolved in 12 cc. 76% alcohol and cooled in ice gave 2nd 1st 0.32 g., m. 50-74°. Recrystallization from 7 cc. 80% alcohol gave 3rd 1st 0.28 g., m. 40-85° and recrystallization from 95% alcohol gave 4th 1st 0.20 g., m. 45-50°. The experiment was abandoned. The ester seems to be formed but is difficult to purify.

Dibasic Acids.

Chlorofumaric Acid.—A mixture of 1.0 g. R, the sodium salt (from 0.35 g. acid + 0.24 g. carbonate) and 15 cc. 63% alcohol was boiled two hours. Glistening tablets were obtained on cooling. The 1st 1st was 0.33 g., m. 138-9° and 2nd 1st 0.02 g., m. 100°. Crystallization of 1st 1st from 50 cc. 76% alcohol gave 2nd 1st 0.30 g., m. 138°. Recrystallized once again the 3rd 1st was 0.27 g., m. 138.5°.

Dibromosuccinic Acid.—One gram reagent dissolved in 10 cc. 95% alcohol was added to the salt (from 0.63 g. acid + 0.24 g. sodium carbonate) in 5 cc. water and the mixture boiled one hour. The solution became amber colored and the white ester which precipitated was kept in solution by addition of 50 cc. 95% alcohol (in portions during the hour). The 1st 1st was 0.22 g., m. 157°. Dissolved in 120 cc. 76% alcohol the 2nd 1st was 0.18 g., m. 167° and 2nd 2nd 0.03 g., m. 100°. Two recrystallizations gave 3rd 1st 0.10 g., m. 178° and 4th 1st was 0.08 g., m. 177.5-8°. Lyman and Reid reported 168°.

Mucic Acid.—The 0.5 g. R, dissolved in 5 cc. 95% alcohol, was added to the sodium salt (from 0.24 g. acid + 0.12 g. carbonate) dissolved in 2.5 cc. water. The ester appears after a few moments' boiling. Fifty cc. 95% alcohol was without effect. The cooled filtrate gave 1st 1st 0.13 g., m. 222°. This was discarded, since the acid melts at 213°. The insoluble part was 0.12 g., which did not melt at 300°. The ester is very soluble in hot water from which it was crystallized. It did not melt at 310°. Lyman and Reid reported failure with this acid.

Camphoric Acid.—The salt (from 0.24 g. acid + 0.12 g. carbonate) in 2.5 cc. water was added to the 0.50 g. R, dissolved in 5 cc. 95% alcohol. On boiling an oil was thrown out, which did not dissolve on the addition of 20 cc. alcohol. After boiling two hours crystallization was very slow.

On standing two days white crystals appeared. The 1st 1st was 0.31 g., m. 71°. This crystallized from 5 cc. 95% alcohol gave 2nd 1st 0.08 g., m. 66.5–67°. This was crystallized from 3 cc. 63% alcohol; 3rd 1st was 0.02 g., m. 66.5°. This ester is very soluble both in 95% and 63% alcohol and requires ice cooling for appreciable crystallization.

***p*-Nitrobenzyl Esters of Aromatic Acids. Monobasic Acids.**

***p*-Chlorobenzoic Acid.**—A mixture of 1 g. R, the sodium salt (from 0.72 g. acid + 0.24 g. carbonate) and 15 cc. 63% alcohol was boiled one hour. An oil which separated during the first few minutes redissolved on addition of 5 cc. 95% alcohol. On further boiling fine, white crystals appeared. Addition of 95% alcohol (10 cc.) did not seem to hinder pptn. of crystals. After boiling one hour the reaction mixture was cooled quickly and crystals filtered off. This gave 1st 1st 0.50 g., m. 129–30°. The filtrate gave an oil on dilution. Recrystallization of 1st 1st from 20 cc. 95% alcohol gave 2nd 1st 0.40 g., m. 128.5° and 2nd 2nd 0.08 g., m. 127.5° (discarded). The 2nd 1st recrystallized again as above gave 3rd 1st 0.33 g., m. 129.5° and 3rd 2nd 0.03 g., m. 128–9°. The 3rd 1st crystallized from 15 cc. 95% alcohol gave 4th 1st 0.30 g., m. 129.5° and 4th 2nd 0.01 g., m. 129.5°.

***m*-Bromobenzoic Acid.**—A mixture of 0.50 g. *p*-nitrobenzyl chloride, the sodium salt (from 0.58 g. acid + 0.13 g. carbonate) and 7.5 cc. 63% alcohol gave a clear solution on boiling. A trace of oil separated during the boiling but dissolved on addition of 95% alcohol. Rapid cooling after boiling one hour gave a nice crop of white crystals, 1st 1st 0.38 g., m. 102.5° and 1st 2nd 0.12 g., m. 63° (discarded). The 1st 1st crystallized from 7 cc. 95% alcohol gave 2nd 1st 0.37 g., m. 105° and a trace of 2nd 2nd, m. 94°. The 2nd 1st recrystallized from 7 cc. 95% alcohol gave 3rd 1st 0.33 g., m. 104.5–105° and 3rd 2nd 0.12 g., m. 104.°

***m*-Nitrobenzoic Acid.**—One-half gram R, the sodium salt (from 0.38 g. acid + 0.12 g. carbonate) and 7.5 cc. 63% alcohol gave after five minutes' boiling an oil which required 20 cc. 95% alcohol for solution. After boiling one hour 10 cc. water were added (to saturation) and cooled rapidly. This gave white crystals 1st 1st 0.20 g., m. 145° and 1st 2nd 0.05 g., m. 90°. The 1st 1st crystallized from 90 cc. 60% alcohol gave 2nd 1st 0.12 g., m. 141.5° and 2nd 2nd 0.03 g., m. 141°. The 2nd 1st recrystallized from 103 cc. 40% alcohol gave 3rd 1st 0.10 g., m. 141.5° and no 3rd 2nd.

***p*-Nitrobenzoic Acid.**—A mixture of 0.50 g. R, the sodium salt (from 0.38 g. acid + 0.12 g. carbonate) and 7.5 cc. 63% alcohol was boiled. Instead of dissolving it seemed as if precipitation took place. It took 25 cc. 95% alcohol to keep ppt. in solution. After boiling one hour water

was added to saturation. Rapid cooling yielded 1st 1st 0.20 g., m. 168° and 1st 2nd, 0.02 g., m. 90°. The 1st 1st crystallized from 30 cc. 95% alcohol gave 2nd 1st 0.13 g., m. 167.5–8° and 2nd 2nd 0.03 g., m. 122°. The 2nd 1st recrystallized from 30 cc. 60% alcohol gave 3rd 1st 0.12 g., m. 168–8.5° and only a trace of 3rd 2nd.

m-Aminobenzoic Acid.—One gram *p*-nitrobenzyl bromide, the sodium salt (from 0.6 g. acid + 0.24 g. carbonate) and 15 cc. 63% alcohol gave on standing overnight (previously to boiling) yellow crystals. On boiling all dissolved to a clear solution, but after about 10 minutes the yellow crystals again appeared. Fifteen cc. 95% alcohol kept them in solution during the hour's boiling. Rapid cooling gave yellow crystals 1st 1st 0.80 g., m. 193–8° and 1st 2nd 0.45 g., m. 180–95°. The 1st 1st and 1st 2nd were combined and crystallized from 25 cc. 63% alcohol. This gave 2nd 1st 0.95 g., m. 200–1° and 2nd 2nd 0.27 g., m. 172° (too close to m. p. of the acid, —174°). The 2nd 1st recrystallized from 22.5 cc. 63% alcohol gave 3rd 1st 0.45 g., m. 201° and 3rd 2nd 0.30 g., m. 201°.

1,2,5-Dihydroxybenzoic Acid.—A mixture of 0.5 g. R, the salt (from 0.36 g. acid + 0.12 g. sodium carbonate) and 7.5 cc. 63% alcohol dissolved to a red solution on boiling. The separated oil required 5 cc. 95% alcohol to dissolve. On rapid cooling yellow leaflets appeared. The 1st 1st was 0.17 g., m. 146° and 1st 2nd 0.12 g., m. 109°. The 1st 1st dissolved in 9 cc. 63% alcohol gave 2nd 1st 0.07 g., m. 160°, and 2nd 2nd m. 160°. The 2nd 1st and 2nd 2nd combined and recrystallized from 3 cc. 95% alcohol gave 3rd 1st 0.02 g., m. 160° and 3rd 2nd 0.02 g., m. 160°.

1,2,4-Dihydroxybenzoic Acid.—To a solution of 0.5 g. R in 5 cc. 95% alcohol was added 0.45 g. sodium salt (from 0.36 g. acid + 0.12 carbonate) dissolved in 2.5 cc. water. On boiling 5 minutes slightly yellow crystals appeared. Eighty cc. 95% alcohol did not hinder the precipitation of the ester. After boiling one hour the cooled solution was filtered. The ppt., 1st 1st, was 0.12 g., m. 187–8°. The filtrate on strong dilution gave 1st 2nd 0.08 g., m. 160° (discarded). The 1st 1st was boiled with 80 cc. 72% alcohol and filtered hot. The insoluble portion was 2nd 1st 0.08 g., m. 188–9°. The cooled filtrate remained clear on dilution.

Another similar mixture was boiled 5 minutes and a portion of the ester precipitated and purified as above melted at 189°.

m-Acetaminobenzoic Acid.—The mixture of 0.50 g. R, the sodium salt (from 0.42 g. acid + 0.12 g. carbonate) and 7.50 cc. 63% alcohol was boiled one hour. Rapid cooling gave fine, slightly yellow needles. The 1st 1st was 0.40 g., m. 170° and 1st 2nd 0.02 g., m. 150°. Crystallization from 50 cc. 38% alcohol gave 2nd 1st 0.35 g., m. 170°. The filtrate on dilution became cloudy but no crystal formed even on standing over-

night. Recrystallization from 10 cc. 95% alcohol gave 3rd 1st 0.23 g., m. 169.5–70° and 3rd 2nd 0.10 g., m. 169.5–70°.

Acetyl-*m*-hydroxybenzoic Acid.—To 0.50 g. R in 5 cc. 95% alcohol was added the sodium salt (from 0.41 g. acid + 0.12 g. carbonate) in 2.50 cc. water. On boiling pptn. of ester occurred. Thirty cc. 95% alcohol were added to keep the ester in solution. On rapid cooling no crystals appeared. Cooled in ice gave 1st 1st 0.15 g., m. 122–6°. The filtrate, on dilution, remained clear after standing overnight (discarded). The 1st 1st crystallized from 40 cc. 72% alcohol gave 2nd 1st 0.13 g., m. 139–40° and only a trace of 2nd 2nd. Recrystallization as above gave 3rd 1st 0.12 g., m. 140° and no 3rd 2nd.

***p*-Toluic Acid.**—On boiling a mixture of 0.50 g. R, the sodium salt (from 0.31 g. acid + 0.12 g. carbonate) and 7.50 cc. 63% alcohol an oil separated. Ten cc. 95% alcohol were added to dissolve it. Rapid cooling after boiling one hour gave 1st 1st 0.30 g., m. 104–5° (fine white needles), and 1st 2nd 0.03 g., m. 100°. Crystallization of 1st 1st from 15 cc. 63% alcohol gave 2nd 1st 0.27 g., m. 104.5°. The filtrate gave only an emulsion.

***p*-Thiol Toluic Acid.**—To 0.50 g. R, dissolved in 5 cc. 95% alcohol, were added 0.35 g. acid, 0.12 g. sodium carbonate and 2.5 cc. water. (The carbonate did not act readily on the acid.) On boiling the mixture a reddish oil separated. Thirty cc. 95% alcohol prevented further precipitation. After boiling one hour, the solution which had assumed a red color gave a reddish precipitate which coagulated in ball-like masses. The 1st 1st was 0.37 g., m. 97° and 1st 2nd 0.07 g., m. 97°. This being too close to the m. p. of the reagent a mixt m. p. (half and half) was 75°. Crystallization of 1st 1st and 1st 2nd from 5 cc. 95% alcohol gave yellow crystals 2nd 1st 0.18 g., m. 97° and 2nd 2nd 0.02 g., m. 97°.

This experiment repeated gave practically the same results.

***o*-Creosotic Acid.**—A mixture of 0.50 g. R, the sodium salt (from 0.35 g. acid + 0.12 g. carbonate) and 7.5 cc. 63% alcohol gave a trace of oil on boiling. Eight cc. of 95% alcohol were sufficient to keep it in solution. An emulsion which formed on rapid cooling gave fine, white crystals when cooled in ice. The 1st 1st was 0.22 g., m. 94–7° and 1st 2nd 0.03 g., m. 60° (a mixture, half reagent and half ester, melted at 87°). The 1st 1st was dissolved in 10 cc. 68% alcohol. An oil was thrown out. The solution was decanted and gave, on cooling, white ball-like mass, 2nd 1st 0.09 g., m. 98°. The filtrate on dilution gave an emulsion which would not crystallize. The oil was dissolved in 3 cc. 95% alcohol. Cooling in ice gave 0.05 g. fine white crystals, m. 98°. This was combined with 2nd 1st and recrystallized from 18 cc. 66% alcohol. Here again there was a tendency for a trace of oil to separate out. One cc. 95% alcohol was added

and solution cooled quickly in ice water. The 3rd 1st was 0.13 g., m. 98.5°. There was no 3rd 2nd. Another mixt. m. p. was 93°.

m-Creosotic Acid.—To 0.25 g. R in 3 cc. 95% alcohol was added the sodium salt (from 0.17 g. acid + 0.06 g. carbonate) in 1.0 cc. water. On boiling a few minutes some ester precipitated. Twenty cc. 95% alcohol, in portions, were added from time to time to keep the ester in solution. Boiled one-half hour and cooled rapidly, copious white crystals precipitated. The 1st 1st was 0.12 g., m. 114° and 1st 2nd 0.03 g., m. 97°. Twenty-eight cc. 95% alcohol were just enough to dissolve the 1st 1st. Cooling gave 2nd 1st 0.07 g., m. 168° and 2nd 2nd 0.04 g., m. 114°. Recrystallized from 50 cc. 57% alcohol gave 3rd 1st 0.05 g., m. 174.5–5°. This recrystallized from 130 cc. 55% alcohol gave 4th 1st 0.04 g., m. 174.5°.

p-Creosotic Acid.—To 0.50 g. R, in 5 cc. 95% alcohol, was added 0.40 g. sodium salt in 2.5 cc. water. Boiling produced beautifully glistening plates which dissolved on addition of 30 cc. 95% alcohol. Slow cooling precipitated long, fine needles. The 1st 1st was 0.30 g., m. 142° and 1st 2nd 0.04 g., m. 130°. The 1st 1st crystallized from 43 cc. 79% alcohol gave fine needles, 2nd 1st 0.25 g., m. 147° and 2nd 2nd 0.02 g., m. 144°. Recrystallization of 2nd 1st from 20 cc. 95% alcohol gave 3rd 1st 0.23 g., m. 147° and 3rd 2nd 0.01 g., m. 144°.

5-Iodosalicylic Acid.—A mixture of 0.50 g. R, in 5 cc. 95% alcohol, and the sodium salt (from 0.61 g. acid + 0.12 g. carbonate) in 2.5 cc. water gave on a few moments' boiling fine, white crystals. Twenty cc. 95% alcohol were sufficient to keep the ester from precipitating. Rapid cooling gave 1st 1st 0.22 g., m. 128–32° and 1st 2nd 0.12 g., m. 90°. Crystallization of 1st 1st from 50 cc. 63% alcohol gave 2nd 1st 0.20 g., m. 139.5° and only a trace of 2nd 2nd. Recrystallized from 45 cc. 63% alcohol this gave 3rd 1st 0.18 g., m. 141° and this crystallized from 26 cc. 80% alcohol gave 4th 1st 0.15 g., m. 141°.

5-Aminosalicylic Acid.—One-half g. R, dissolved in 5 cc. 95% alcohol, and sodium salt (from 0.35 g. acid + 0.12 g. carbonate) in 2.5 cc. water were mixed and subjected to the usual process. The ester began to separate on boiling. Twenty-five cc. 95% alcohol kept it in solution. Cooling as usual gave yellow crystals. (The mother liquor was red.) The 1st 1st was 0.42 g., m. 205°, and 1st 2nd 0.13 g., m. 215°. The 1st 1st recrystallized from 45 cc. 70% alcohol gave 2nd 1st 0.30 g., m. 201° and 2nd 2nd, 0.03 g., m. 201°. Recrystallization of the above, combined from 27 cc. 70% alcohol, gave 3rd 1st 0.23 g., m. 200.5–1° and only a trace of 3rd 2nd.

Acetylsalicylic Acid.—The usual reaction mixture 0.5 g. R and the sodium salt (from 0.41 g. acid + 0.12 g. carbonate) in 7.5 cc. 63% alcohol was

boiled one hour. During the boiling an oil which separated was dissolved on addition of 15 cc. 95% alcohol. Cooling gave white crystals. The 1st 1st was 0.15 g., m. 90°. The filtrate on dilution became oily. Crystallization from 15 cc. 63% alcohol gave 2nd 1st 0.13 g., m. 90–0.5°.

Anisic Acid (*p*-Methoxybenzoic Acid).—To the usual amount of the reagent dissolved in 5 cc. 95% alcohol was added the sodium salt (from 0.35 g. acid + 0.12 g. carbonate) dissolved in 2.5 cc. water. The ester began to precipitate but 30 cc. alcohol (95%) added from time to time served to keep the ester in solution. White needles were thrown out on cooling. The 1st 1st was 0.38 g., m. 131°. The 1st 2nd, only a trace, m. 128°. Crystallization from 12 cc. 95% alcohol gave 2nd 1st 0.35 g., m. 132° and 2nd 2nd 0.02 g., m. 122°. Recrystallization from 25 cc. 63% alcohol gave 3rd 1st 0.28 g., m. 132° and 3rd 2nd 0.04 g., m. 129°.

Vanillic Acid.—A mixture of 0.50 g. R and the sodium salt (from 0.39 g. acid + 0.12 g. carbonate) in 75 cc. 63% alcohol gave a reddish solution on boiling. The cooled solution yielded white crystals. The 1st 1st was 0.47 g., m. 135–40° and 1st 2nd 0.10 g., m. 125°. Crystallization from 15 cc. 63% alcohol gave 2nd 1st 0.18 g., m. 125° and 2nd 2nd 0.18 g., m. 136°. The 1st 2nd was combined with these latter two and all recrystallized from 15 cc. 63% alcohol. This gave 3rd 1st, 0.35 g., m. 132° and 3rd 2nd 0.05 g., m. 128°. Recrystallization of 3rd 1st from 12 cc. 63% alcohol gave 4th 1st 0.25 g., m. 140–1° and 4th 2nd 0.03 g., m. 140–1°. Another crystallization as above gave 5th 1st 0.20 g., m. 140–1° and 5th 2nd 0.03 g., m. 140–1°. This compound seems to decompose at the melting point.

Piperic Acid.—To one gram reagent in 10 cc. 95% alcohol was added the sodium salt (from 1.01 g. acid + 0.24 g. carbonate) dissolved in 5 cc. water. Boiling a few moments produces a ppt. of the ester. Forty cc. 95% alcohol did not hinder precipitation. After one hour, the solution was filtered hot. The insoluble portion was 0.70 g., m. 145°. The filtrate on cooling gave 1st 1st 0.30 g., m. 140° and no 1st 2nd. Combination of the insoluble portion with 1st 1st and crystallization from 100 cc. 76% alcohol gave 2nd 1st 0.65 g., m. 145° and 2nd 2nd 0.2 g., m. 143°. Recrystallization from 20 cc. 80% alcohol gave 0.12 g., m. 145°.

Gallic Acid.—The mixture 0.50 g. R and the sodium salt (from 0.43 g. acid + 0.12 carbonate) in 7.5 cc. 63% alcohol was boiled one hour. The solution turned reddish. An oil which precipitated redissolved on addition of 10 cc. 95% alcohol. Cooling under tap did not induce crystallization. Ice cooling produced a red gummy substance. Crystallization from 5 cc. 95% alcohol gave 1st 1st 0.12 g., m. 210–5°. Recrystallization from 15 cc. 33% alcohol gave 2nd 1st 0.06 g., m. 226°. No 2nd 2nd on dilution of filtrate. Recrystallization from 7 cc. 33% alcohol gave 3rd 1st 0.03

g., m. 226°. Gallic acid is given as melting 226°. The acid used melts at 242° and a mixt. m. p. was 218°. Hydrolysis of the ester must have taken place.

o-Nitrocinnamic Acid.—As usual the reaction mixture of 0.50 g. R and the sodium salt (from 0.45 g. acid + 0.12 g. carbonate) in 7.5 cc. 63% alcohol was boiled. Precipitation of the ester was prevented only on addition of 30 cc. 95% alcohol. Rapid cooling produced fine, white crystals 1st 1st 0.53 g., m. 140–210°, and 1st 2nd 0.05 g., m. 230°. Crystallization from 25 cc. 95% alcohol gave 2nd 1st 0.40 g., m. 120° and 2nd 2nd 0.07 g., m. 234°. (The acid melts at 237°.) Recrystallization from 50 cc. 66% alcohol gave 3rd 1st 0.30 g., m. 132° and 3rd 2nd 0.06 g., m. 122°. Recrystallization of 0.15 g. 3rd 1st from 10 cc. 95% alcohol gave 0.14 g., m. 132°, and the other 0.15 g., crystallized from 18 cc. 66% alcohol, gave 0.13 g., m. 132°.

m-Nitrocinnamic Acid.—A mixture corresponding to the above produced, after boiling a few minutes, an ester which was even more insoluble than the ortho compound. It required 115 cc. 95% alcohol to keep it in solution. The 1st 1st was 0.40 g., m. 174°. The filtrate remained clear on dilution. Of the 1st 1st 0.10 g. was dissolved in 35 cc. 95% alcohol. Cooling gave 2nd 1st 0.06 g., m. 173.5° and 2nd 2nd 0.02 g., m. 173.5°. Recrystallization of these from 30 cc. 95% alcohol gave 3rd 1st 0.05 g., m. 173.5–4° and 3rd 2nd 0.02 g., m. 173°.

p-Nitrocinnamic Acid.—A similar experiment (see ortho compound) with this acid gave a difficultly soluble ester. The 1st 1st was 0.40 g., m. 185° and 1st 2nd 0.07 g., m. 177°. The former was boiled with 70 cc. 95% alcohol and was only partly soluble. The solution was filtered hot and gave, on cooling, 2nd 1st 0.13 g., m. 186.5° and 2nd 2nd 0.05 g., m. 181°. The insoluble portion was 0.15 g., m. 186.5°. A portion of the 2nd 1st was recrystallized from 95% alcohol and melted sharply at 186.5°.

Coumaric Acid.—To one gram R, dissolved in 10 cc. 95% alcohol, was added the sodium salt (from 0.76 g. acid + 0.24 g. carbonate) dissolved in 5 cc. water. The solution remained clear throughout the boiling. Rapid cooling yielded yellow needles. The 1st 1st was 0.70 g., m. 150–2°, the 1st 2nd 0.05 g., m. 128–32°. Solution of 1st 1st in 20 cc. 95% alcohol gave 2nd 1st 0.55 g., m. 153° and 2nd 2nd 0.10 g., m. 154.5°. Combination of these and recrystallization from 20 cc. 95% alcohol gave 3rd 1st 0.40 g., m. 152.5–3° and 3rd 2nd 0.10 g., m. 152.5–3°.

β-Hydroxynaphthoic Acid.—A mixture of 0.50 g. R, the salt (from 0.44 g. acid + 0.12 g. sodium carbonate) and 15 cc. 63% alcohol when boiled produced an emulsion. This dissolved, on addition of 15 cc. 95% alcohol, to an amber-colored solution. Twenty cc. alcohol (in portions) were then added to keep the yellow ester from precipitating. After the

boiling period 5 cc. water saturated the solution. The 1st 1st was 0.27 g., m. 154-5°. Dilution of the filtrate gave an emulsion which would not crystallize. Crystallization from 80 cc. 70% alcohol gave 2nd 1st 0.18 g., m. 154-5°. Recrystallization from 50 cc. 76% alcohol gave 3rd 1st 0.15 g., m. 163-4° and 3rd 2nd 0.02 g., m. 154°. The 3rd 1st was recrystallized from 40 cc. 67% alcohol and a lighter yellow ester obtained. The 4th 1st was 0.07 g., m. 164° and 4th 2nd, 0.06 g., m. 163-4°. This ester is considerably soluble in water.

Saccharin (Benzoic Sulfinid).—One-half gram reagent, the sodium salt (from 0.42 g. saccharin + 0.12 g. carbonate) and 7.5 cc. 63% alcohol gave a clear solution. Fine, white needles obtained. The 1st 1st was 0.30 g., m. 155° and 1st 2nd 0.04 g., m. 89°. Crystallization from 45 cc. 42% alcohol gave 2nd 1st 0.20 g., m. 157° and 2nd 2nd 0.03 g., m. 90°. Recrystallization from 25 cc. 95% alcohol gave 3rd 1st 0.10 g., m. 174° and 3rd 2nd 0.02 g., m. 89°. Recrystallized again from 15 cc. 95% alcohol gave 4th 1st 0.08 g., m. 174.5°. The ester is only slightly sweet.

Polybasic Acids.

Isophthalic Acid.—The salt (from 0.38 g. acid + 0.24 g. sodium carbonate) in 5 cc. water was added to one gram of the reagent dissolved in 10 cc. 95% alcohol. The solution, at first clear, gave an insoluble, white ester. No attempt was made to dissolve it during the boiling. On cooling the 1st 1st was 0.20 g., m. 200°. Dilution of the filtrate gave an emulsion but no crystals (on standing overnight). The difficultly soluble ester was boiled with 20 cc. 95% alcohol and filtered hot. The residue was 0.16 g., m. 202°. The filtrate gave on slight dilution a cloudiness which disappeared on further dilution. The ester is somewhat soluble in very dilute alcohol. Another treatment with 20 cc. alcohol as above gave 0.14 g., m. 202.5°. Lyman and Reid made this ester but did not attempt its purification.

Terephthalic Acid.—The reaction mixture as above with this acid gave at first a clear solution. However, here too, boiling a few moments caused precipitation of the ester. Sixty cc. 95% alcohol seemed to have no effect on it. After boiling one-half hour the mixture was treated as in previous case. The 1st 1st was 0.22 g., m. 262.5-3°. The 1st 2nd was 0.24 g., m. 90-110° (discarded). Purification of the 1st 1st by boiling with 95% alcohol and with dilute alcohol gave 0.18 g., m. 263-3.5°. Another experiment using half the amounts and boiling one hour gave 1st 1st 0.13 g., m. 263° and 1st 2nd 0.12 g., m. 190°. Purified by boiling with dilute alcohol the 1st 1st gave 2nd 1st 0.12 g., m. 263-3.5°. This ester is among the most insoluble ones so far made.

4,5-Dichlorophthalic Acid.—The reaction mixture, the salt (from 0.54 g. acid + 0.24 g. sodium carbonate) figured for one g. R, gave slightly

yellow needles which are very insoluble. One hundred cc. 95% alcohol kept all ester in solution. The mixture was boiled two and one-half hours. Cooling gave 1st 1st 0.53 g., m. 146–9° and 1st 2nd 0.05 g., m. 146°. These were combined and boiled with 100 cc. 95% alcohol which seemed to dissolve only part. The residue was 0.08 g., m. 157°. The filtrate cooled gave 2nd 1st 0.30 g., m. 148–9° and 2nd 2nd 0.06 g., m. 136–7°. Combination of 2nd 1st with the insoluble, 0.08 g., and boiling with portions of 95% and dilute alcohol gave 3rd 1st 0.20 g., m. 164° and 3rd 2nd 0.05 g., m. 151°. This repeated gave 4th 1st 0.13 g., m. 164–4.5° and 4th 2nd 0.05 g., m. 159–60°. Boiling two and one-half hours is evidently not beneficial.

Tetrachlorophthalic Acid.—In this experiment, the salt (from 0.35 g. acid + 0.12 g. sodium carbonate) was figured from 0.5 g. R. Boiling first produced an emulsion which dissolved on addition of 28 cc. 95% alcohol. Further boiling yielded beautifully glistening needles. It was boiled one-half hour. The 1st 1st was 0.14 g., m. 176°. The filtrate gave a tarry substance on dilution (discarded). Purification by boiling with 50 cc. 95% alcohol gave 2nd 1st 0.10 g., m. 180–1°. This when boiled with 30 cc. 63% alcohol and filtered hot left 0.05 g., m. 180–1° and the cooled filtrate gave 0.02 g., m. 180–1°. It is evident that these phthalic esters are very insoluble in 95% alcohol but somewhat soluble in more dilute alcohol, probably with hydrolysis, as the addition of water does not precipitate all of it.

3-Nitrophthalic Acid.—A mixture of 0.50 g. R, the salt (from 0.25 g. acid + 0.12 g. sodium carbonate) and 7.5 cc. 63% alcohol gave crystals of the ester after boiling 15 minutes. Alcohol did not seem to hinder precipitation of ester. After boiling one hour the mixture was cooled and filtered. The insoluble residue was 0.18 g., m. 189°. The filtrate gave no crystals on dilution. The insoluble part boiled with several portions of 63% and 95% alcohol gave 0.12 g., m. 189.5–90°.

Mellitic Acid.—The sodium salt (from 0.26 g. acid + 0.24 g. carbonate) was figured from 1 g. R. On boiling the usual mixture, fine, glassy octahedra crystals were formed. Boiled two hours, filtered hot. The insoluble part was 0.10 g. and did not melt at 300°. The filtrate gave 1st 1st 0.32 g., m. 97° and 1st 2nd 0.22 g., m. 97°. These were discarded since with the reagent they gave a mixt. m. p. 98°. The insoluble part was boiled with 75 cc. 95% alcohol. Filtered hot. The insoluble was 0.05 g., and filtrate gave 0.03 g., which did not melt at 300°.

p-Nitrobenzyl Esters Which Are Liquids.

Salts of oleic, euracic, linoleic, asparaginic, ethylglycollic, valeric, β -oxybutyric, dibromoacetic, tribromoacetic, mono- and dichloroacetic

acids gave oily products which would not solidify. Trichloroacetic gave a trace of ester melting at about 80° . Aconitic gave a non-weighable amount, m. 76° and aspartic gave a trace m. about 162° . These latter were tried several times with poor success.

Sulfonic Acids.

Sulfonic acids could not be induced to form esters. The Na and Ag salts were boiled in aqueous, dilute and strong alcoholic solutions without forming any appreciable quantity of esters. Sealing the salts with the reagent in small tubes and heating to fusion gave no results.

The results are brought together in tabular form, the first and second columns giving the weights of the first and second crops of crystals, the fifth and sixth the first and final melting points, and the eighth and ninth the approximate number of cubic centimeters of hot and cold alcohol, of the strength given in the seventh column, required to dissolve 1 g. ester. Blank spaces in column under 1st 2nd mean either that an emulsion was produced on dilution of filtrate, or that no crystals appeared on standing for some time. The figures in parenthesis indicate 1st 2nds which were mostly unchanged reagent.

The figures in columns under "Alc.," "Hot," "Cold" represent the solubilities of the ester in the impure form. The esters are somewhat hydrolyzed on boiling. The presence of impurity either increases or decreases the solubility, and the figures are therefore only approximate. The sodium bromide in the original solution doubtless "salts out" some of the ester. The figures under "Hot" were obtained by dissolving the 1st 1st in 95% alcohol and then adding water to saturation. The figures under "Cold" were gotten by taking the difference between 1st 1st and 2nd 1st (e. g., if 0.10 g. 1st 1st dissolved in 20 cc. 63% hot alcohol gives on cooling 0.05 g. 2nd 1st., then the solubility in hot alcohol is 1.0 g. in 200 cc. and in cold alcohol 1.0 g. in 400 cc.). The figures in the last two columns are fairly accurate. The pure ester was weighed to the 3rd decimal, dissolved carefully in 95% alcohol, cooled, filtered on a weighed filter paper and dried over a radiator. Where the ester was practically insoluble a weighed portion was boiled with about 25 cc. 95% alcohol and filtered hot. Blank spaces are due to not having enough of the ester to get fair results.

TABLE III.
Yields, Melting Points and Solubilities of Esters.

Esters.	1st 1st. G.	1st 2nd. G.	Total. G.	Calc. G.	Melting point.		Alo. %.	Hot. C.	Cold. C.	95% alcohol.	
					First.	Final.				Hot. C.	Cold. C.
Monobromoacetate.....	0.07	0.07	0.63	75-80°	88-9°	12	471	1100
Benzilate.....	0.55	0.55	0.84	96°	99.5°	95	24	100	7.5	30
Leucate.....	0.13	0.13	0.61	198-9°	184-5°	50	192	833
Phenylalanate.....	0.25	(0.39)	0.25	0.69	221-3°	221.5°	2000	2860
Alanate.....	0.07	0.07	0.51	210-30°	228-30°	95	500	1375
Levulinat.....	0.30	0.10	0.40	0.57	58-60°	60.5-1°	34	32	162
Oxyisobutyrate.....	0.08	0.71	0.79	1.10	80.5°	80.5°	95	6.3
α -Aminobutyrate.....	0.10	0.10	0.20	0.55	221°	222-3°	74	400	666
Urate.....	0.39	(0.20)	0.39	0.78	>300°	>305°	80	428	1670
Pyromucate.....	0.30	0.07	0.39	0.57	131°	133.5°	70	43	430	28	710
Cyanourate.....	0.18	0.18	0.70	284°	284°	95	666	1000	4000
Stearate(?).....	0.12	0.12	0.97	>285°	>285°
Palmitate.....	0.40	0.40	0.90	60-70°	42.5°	80	30	43
Chlorofumarate.....	0.33	0.02	0.35	0.96	138°	138.5°	76	151	1666	330	1100
Dibromosuccinate.....	0.22	0.22	1.24	157°	177.5°	76	545	3000	415	2250
Mucate.....	0.12	(0.13)	0.12	0.55	>300°	>310°
Camphorate.....	0.31	0.31	0.55	71°	66.5°	95	16	23
<i>p</i> -Chlorobenzoate.....	0.50	0.50	1.34	130°	129.5°	95	40	200	22	770
<i>m</i> -Bromobenzoate.....	0.38	(0.12)	0.38	0.90	102.5°	104.5°	95	18	700	13	228
<i>m</i> -Nitrobenzoate.....	0.20	(0.05)	0.20	0.69	145°	141.5°	60	450	1125	130	1860
<i>p</i> -Nitrobenzoate.....	0.20	0.02	0.22	0.69	168°	168.5°	60	230	3000	157	700
<i>m</i> -Aminobenzoate.....	0.80	0.45	1.25	1.26	193-8°	201°	63	20	83	19	565

TABLE III (continued).

Esters.	1st 1st. G.	1st 2nd. G.	Total G.	Calc. G.	Melting point.		Alc. %.	Hot. Cc.	Cold. Cc.	95% alcohol	
					First.	Final.				Hot. Cc.	Cold. Cc.
1,2,5-Dihydroxybenzoate.....	0.17	(0.12)	0.17	0.68	146°	160°	63	53	90
1,2,4-Dihydroxybenzoate.....	0.12	0.08	0.20	0.68	187-8°	188-9°	80	2000	1095	1770
m-Acetaminobenzoate.....	0.40	0.02	0.42	0.74	170°	169.5-70°	38	125	1000	30	230
Acetyl-m-oxybenzoate.....	0.15	0.15	0.73	122-6°	140°	72	266	2000	320	3630
p-Toluate.....	0.30	0.03	0.33	0.62	104-5°	104.5°	63	50	500	15	178
p-Thiol toluate.....	0.37	0.07	0.44	0.67	97°	97°	95	13	26	19	235
o-Cresotate.....	0.22	(0.03)	0.23	0.67	94-7°	98.5°	68	45	125	20	95
m-Cresotate.....	0.12	(0.03)	0.12	0.33	114°	174°	95	280	672	700
p-Cresotate.....	0.30	0.04	0.34	0.67	142°	147°	79	143	860	62	600
5-Iodosalicylate.....	0.22	(0.12)	0.22	0.93	128-32°	141°	63	230	2500	100	725
5-Aminosalicylate.....	0.42	0.13	0.55	0.66	205°	200.5°	70	170	460	30	300
Acetylsalicylate.....	0.15	0.15	0.73	90°	90.5°	63	100	750	15	75
Anisate.....	0.38	0.38	0.67	131°	132°	95	31	400	40	675
Vanillate.....	0.47	0.10	0.57	0.71	135-40°	140-1°	63	34	100	15	85
Piperate.....	1.00	1.00	1.64	140-5°	145°	76	100	280	210	2840
o-Nitrocinnamate.....	0.53	(0.05)	0.53	0.77	140-210°	132°	66	125	500	60	1000
m-Nitrocinnamate.....	0.40	0.40	0.77	174°	174°	95	350	875	380	7600
p-Nitrocinnamate.....	0.40	0.07	0.47	0.77	185°	186.5°	95	540	1000	260	2600
Coumarate.....	0.70	0.05	0.75	1.40	150-2°	152.5°	95	29	133	5	52
Hydroxynaphthoate.....	0.27	0.27	0.76	154°	164°	70	300	888	280	1395
Saccharate.....	0.30	0.04	0.34	1.04	155°	174.5°	42	150	450	130	2540
Isophthalate.....	0.20	0.20	1.00	200°	202.5°	95	500	2450	2975
Terephthalate.....	0.22	0.24	0.46	1.00	263°	263.5°	95	1000	2400	2740
4,5-Dichlorophthalate.....	0.53	0.05	0.58	1.17	146-9°	164.5°	95	286	2000	263	2000
Tetrachlorophthalate.....	0.14	0.14	0.67	176°	180-1°	63	600	1000	1000	4285
3-Nitrophthalate.....	0.18	0.18	0.66	189°	189.5°	1020	3840
Mellitate(?).....	0.10	(0.54)	0.10	1.26	>300°	>300°	415

Separation of Acids from Other Acids.

Acetic and Formic Acids.—Two grams *p*-nitrobenzyl iodide were added to 0.47 g. potassium acetate and 0.37 g. potassium formate (excess used in each being 0.10 g.) and to this 30 cc. 63% alcohol. The mixture was boiled two hours. (Previous experiments of one hour's boiling gave poor results.) On cooling 60 cc. water were added and the emulsion produced gave, on ice cooling, long plates weighing 0.50 g., m. 73°. The filtrate remained clear on dilution. Crystallization of the above from 15 cc. 63% alcohol gave 2nd 1st 0.28 g., m. 76.5° and 2nd 2nd 0.05 g., m. 76°. Combination and recrystallization gave 3rd 1st 0.27 g., m. 78° and 0.03 g., m. 75–8°. The melting point of *p*-nitrobenzyl acetate is 78°. The formate, however, could not be isolated.

Several attempts using the bromide gave comparable but poorer yields of the acetate. An attempt in which the silver salts were used proved a failure. It was thought that partial neutralization of the mixture of acids (taking advantage of the stronger acidity of formic acid) might give the salt of formic acid and that this could be then removed as the ester, leaving the acetic acid or most of it in the mother liquor, to be sought for afterwards. This too proved unsuccessful.

Acetic and Isophthalic Acids.—Two g. of the reagent, the calculated amounts of the acids (0.10 g. each, in excess, used), the sodium carbonate and 30 cc. 63% alcohol were boiled half an hour. Precipitation of the insoluble *p*-nitrobenzylisophthalate took place on boiling a few moments. The precipitate was filtered hot. The undissolved portion was 0.52 g. in 202–2.5° (m. p. of *p*-nitrobenzylisophthalate is 202.5°). On cooling the filtrate gave 0.13 g., m. 170°, which when recrystallized gave 0.05 g., m. 115°. This was probably mostly reagent (discarded). The filtrate was boiled a half-hour longer and on dilution gave 0.60 g., m. 55°. Crystallization from 95%, 63% and 50% alcohol did not give a pure substance. The m. p. in each case was 58–60° (discarded). It is easy to identify the isophthalic but not the acetic acid.

Tartaric and Isophthalic Acids.—As in other mixtures the isophthalate separated. The undissolved portion was 1.0 g., m. 194° and filtrate gave 0.30 g., m. 150–194°. The insoluble part was boiled with 10 cc. 95% alcohol and filtered hot. The residue, 0.67 g., m. 202–3°. The filtrate gave 0.18 g., m. 160–80°. This was combined with the above 0.3 g. and crystallized from 95% alcohol gave 0.27 g., m. 163–4°. Several crystallizations from 63 and 95% alcohol failed to change the m. p. A mixt. m. p. with the pure tartrate was 161°. The pure tartaric ester melts at 163°. Hence tartaric and isophthalic acids may be separated and both identified.

Benzoic and Acetic Acids.—The reagent in this case was the iodide instead of the bromide. The usual reaction mixture was boiled one hour. The 1st 1st was 0.58 g., m. 88.5–89°; the 1st 2nd 0.12 g., m. 73° and an oil which had separated was decanted and gave, on cooling, 0.26 g., m. 88.5–89°. Combination of 1st 1st and this gave, from 19 cc. 80% alcohol, 0.52 g., m. 89° and 0.65 g., m. 86°. The 1st 2nd, crystallized from 5 cc. 95% alcohol, gave 0.05 g., m. 75° (discarded). The benzoic acid can be readily identified.

Benzoic and Citric Acids.—The mixture 2 g. R and the calculated amount (0.10 g. excess used) sodium salts of the acids was boiled in 63% alcohol one hour. On cooling an oil separated which crystallized, giving 0.35 g., m. 79°. The solution gave fine, glistening needles 0.72 g., m. 87°. Recrystallization of this gave 0.42 g., m. 88.5–9° (the benzoate melts at 89°). The filtrate from this gave 0.07 g., m. 85°. This was combined with the 0.31 g. melting at 79° and crystallized several times without definite results, the melting point being 84–86°. The benzoic is readily identified.

Benzoic and Tartaric Acids.—The mixture corresponding to the above gave 1st 1st 1.45 g., m. 89–136°. Boiled with 15 cc. 63% alcohol gave 0.22 g., m. 125° and an oil. The 0.22 g. was crystallized from 20 cc. 55% alcohol and gave 0.10 g., m. 89–95°. The oil was crystallized from 10 cc. 95% alcohol and gave 1.03 g., m. 90–94°. Boiling with 63% alcohol gave 0.12 g., m. 89–92° and an oil left which crystallized from 95% alcohol gave 0.56 g., m. 89–92°. All of these were then combined and recrystallized from 63% alcohol. A trace of oil which separated was decanted. The precipitated crystals weighed 0.45 g., m. 89–89.5°. The filtrate gave an emulsion on dilution. Polybasic acids usually give rather poor yields of the esters. The amount of *p*-nitrobenzyl tartrate present appears to have been diminished by hydrolysis during the crystallizations.

Benzoic and Isophthalic Acids.—The calculated acids, carbonate and 2 g. R, were boiled in 63% alcohol one hour. The difficultly soluble isophthalate again ppts. Cooled and filtered, the 1st 1st was 1.35 g., m. 170–80°. (Probably best filtered hot to keep benzoate from precipitating.) The 1st 2nd was 0.45 g., m. 85–150°. The 1st 1st was boiled with 95% alcohol and filtered hot. This gave 0.60 g., m. 202–3°. (Isophthalate melts 202–2.5°.) The filtrate gave 0.46 g., m. 140–50°. This was combined with 1st 2nd and attempts to purify this proved fruitless, the m. p. remaining 120–30° (discarded). The isophthalate is readily identified.

Benzoic and *p*-Toluenesulfonic Acids.—The reaction mixture, figured on 2 g. R, was boiled 2 hours. The 1st 1st was 1.05 g., m. 92°. The 1st 2nd 0.35 g., m. 89–90°. This latter was recrystallized from 15 cc. 63% alcohol and gave 0.20 g., m. 89.5° and 0.08 g., m. 85°. The 1st 1st

crystallized from 20 cc. 80% alcohol gave 2nd 1st 0.38 g., m. 89° and 2nd 2nd 0.41 g., m. 90-1°. This with above 0.20 g. from 5 cc. 95% alcohol gave 0.30 g., m. 89-9.5° and 0.20 g., m. 90°. The former is practically pure benzoate while the latter 0.20 g. evidently contained some of the reagent. The ester of the sulphonic acid was not formed so the benzoic acid is readily identified.

Phenylalanin and α -Amidobutyric Acid.—Although the *p*-nitrobenzyl esters of these two acids melt at about the same temperature (221-1.5° and 222-3°, resp.), the difference in solubilities (Table III) suggested the possibility of a separation. A mixture was therefore boiled two hours. No attempt was made to dissolve the precipitating crystals. The undissolved part was 0.55 g. melting, with decomposition, at 220-1°. The filtrate gave 0.52 g., m. 125°. (This recrystallized proved to be mostly reagent.) The less soluble part was boiled with 40 cc. 74% alcohol (see experiment α -amidobutyric acid). The insoluble was 0.50 g., m. 220-1°; the filtrate gave an emulsion only and was discarded.

A mixt m. p. with *p*-nitrobenzyl phenylalanate was 219°, with *p*-nitrobenzyl α -amidobutyrate 214°. The ester is therefore the phenylalanate.

***o*- and *p*-Nitrocinnamic Acids.**—Table III shows that these may be separated according to solubilities. The reaction mixture after two hours' boiling gave 1st 1st 1.15 g., m. 135-157° and 1st 2nd 0.32 g., m. 99-105° (reagent). The 1st 1st was boiled with 30 cc. 95% alcohol and filtered hot. The insoluble was 0.62 g., m. 170-78° and filtrate gave 0.35 g., m. 120-30°. This was recrystallized several times from dilute and 95% alcohol with the m. p. remaining 115-20°. The above 0.62 g. was crystallized from 100 cc. 95% alcohol and gave 0.37 g., m. 186-6.5° (*p*-nitrobenzyl-*p*-nitrocinnamate melts at 186.5°) and 0.22 g., m. 120-35° (discarded). Another experiment gave practically the same results. The para acid is readily identified in presence of the ortho.

***o*- and *m*-Nitrocinnamic Acids.**—The solubilities of the esters vary widely and their separation was attempted. The sodium salts were dissolved in 3 cc. water, 1 g. R and 30 cc. 95% alcohol added (should keep all ortho ester in solution). The precipitate which appeared on boiling was not redissolved. After boiling one-half hour it was filtered hot. The insoluble was 0.48 g., m. 174°. (A mixt m. p. with the meta ester was 173°.) The cooled filtrate gave 0.50 g., m. 115° and on dilution 0.20 g., m. 170-200°. This latter on successive crystallizations carried the m. p. toward 200° (free acid). The 0.50 g., m. 115° gave a mixture, melting about 125°, from alcohol, ether and benzene as solvents (discarded). The meta acid is readily identified in presence of the ortho.

Benzoic and Salicylic Acids.—No great difficulty was met with in the separation of the benzoate from the salicylate. Two grams R, 0.75 g. potassium benzoate and 0.85 g. sodium salicylate were boiled one hour in 20 cc. 63% alcohol. On cooling the 1st 1st was 1.52 g., m. 83°. Crystallized from 10 cc. 95% alcohol gave 2nd 1st 1.18 g., m. 86°. This from 15 cc. 80% alcohol gave 3rd 1st 0.60 g., m. 88.5–9°, and 2nd 2nd 0.23 g., m. 83–85°. Recrystallized again the m. p. was 85°. The benzoic ester is readily obtained pure from the mixture.

Another experiment gave 1st 1st 2.20 g., m. 85° and 1st 2nd 0.15 g., m. 80°.

The salicylate being a phenol it was hoped to separate it from the benzoate as follows: The mixture of esters was dissolved in ether and an aqueous solution of NaOH (figured on the salicylate present) added. The sodium salt of the salicylate is precipitated but should dissolve on addition of water. The ethereal extract on evaporation gave the benzoate melting 89°. The aqueous portion on acidification should give the salicylate. Out of four attempts one gave a substance m. 95–96°. (The salicylate melts 96.3° (Lyman).) The others gave what seemed to be the sodium salt. In each case the benzoate was readily obtained.

Tartaric and Oxalic Acids.—A mixture of 2 g. R and the sodium salts of tartaric and oxalic acids boiled in 30 cc. 63% alcohol gave 1st 1st 0.27 g., m. 162° (tartrate melts at 163° (Reid)). When this was boiled with portions of 95% alcohol the melting point went down to 161.5°. A mixt. m. p. with pure tartrate was 161°. Tartaric acid can be readily identified in the presence of oxalic acid.

Mixtures That Gave Negative Results.—Oxalic and citric acids and 1,2,5- and 1,2,4-dihydroxybenzoic acids.

Discussion of Results.

The results obtained show that *p*-nitrobenzyl bromide is a valuable reagent for the identification of acids. Excellent results have been obtained with most of the aromatic acids. With the aliphatic acids, however, more difficulties are encountered as the esters of many of the monobasic acids are oils. The results show that 0.5 g., or even 0.25 g., of the reagent is quite sufficient for a determination.

Lyman and Reid prepared the ester of isophthalic acid but did not give its melting point. This preparation has been repeated and the ester found to melt at 202.5°. They did not obtain the esters of levulinic and mucic acids. These have now been made but the mucic acid derivative does not melt at 310°, and was abandoned. The melting point of *p*-nitrobenzyl *m*-amino-benzoate has been found to be 201° instead of 198.3° and that of *p*-nitrobenzyl-dibromosuccinate 177.5–78°, instead of 168°, as reported by Lyman and Reid.

A beginning has been made on the identification of acids in mixtures and some results of interest have been obtained. Benzoic acid is readily identified by this method, in the presence of acetic, tartaric, citric, salicylic and *p*-toluene sulphonic acids. The difficultly soluble ester of isophthalic acid is readily separated from the acetate, benzoate and tartrate. Some *p*-nitrobenzyl esters, which when alone showed great differences in solubility, could not be separated by a reasonable number of crystallizations.

Summary.

Of 64 carboxylic acids studied 50 gave crystalline esters, of which 2 did not melt at 300°, and 14 gave oils. Uric acid gave a compound which did not melt at 305°. Salts of sulfonic acids do not react with the reagent.

The method has been applied with some success to the identification of acids in mixtures.

The following *p*-nitrobenzyl esters have been prepared: $R = -CH_2-C_6H_4NO_2$.

p-Nitrobenzyl-monobromoacetate, $CH_2BrCO_2CH_2C_6H_4NO_2$, m. 88–9°.

Benzilate, $(C_6H_5)_2 : C(OH)CO_2R$, m. 99.5°.

Leucate, $CH_3(CH_2)_5CH(NH_2)CO_2R$, m. 184–5°.

Phenylalanate, $C_6H_5CH_2CH(NH_2)CO_2R$, m. 221.5°.

Alanate, $CH_3CH(NH_2)CO_2R$, m. 228–30°.

Levulinate, $CH_3COCH_2CH_2CO_2R$, m. 60.5–61°.

Hydroxyisobutyrate, $(CH_3)_2C(OH)CO_2R$, m. 80.5°.

α -Aminobutyrate, $CH_3CH_2CH(NH_2)CO_2R$, m. 222–3°.

Urate, $C_5H_5N_4O_9R (?)$, m. >305°.

Pyromucate, $C_4H_5O_7CO_2R (?)$, m. 133.5°.

Cyanourate, $C_2N_3H_3O_3R (?)$, m. 284°.

Stearate, $CH_3(CH_2)_{16}CO_2R (?)$, m. >285°.

Palmitate, $CH_3(CH_2)_{14}CO_2R$, m. 42.5°.

Chlorofumarate, $R.O_2C.CH.C.ClCO_2R$, m. 138.5°.

Dibromosuccinate, $(.CHBrCO_2R)_2$, m. 177.5°.

Mucate, $RO_2C.(CH(OH))_4.CO_2R$, m. >310°.

Camphorate, $C_{10}H_{14}(CO_2R)_2$, m. 66.5°.

p-Chlorobenzoate, $Cl.C_6H_4.CO_2R$, m. 129.5°.

m-Bromobenzoate, $Br.C_6H_4.CO_2R$, m. 104.5°.

m-Nitrobenzoate, $NO_2C_6H_4.CO_2R$, m. 141.5°.

p-Nitrobenzoate, $NO_2C_6H_4.CO_2R$, m. 168.5°.

m-Aminobenzoate, $NH_2C_6H_4.CO_2R$, m. 201°.

1,2,5-Dihydroxybenzoate, $(OH)_3C_6H_3.CO_2R$, m. 160°.

1,2,4-Dihydroxybenzoate, $(OH)_3C_6H_3.CO_2R$, m. 188–9°.

m-Acetaminobenzoate, $(C_2H_5O)NH.C_6H_4.CO_2R$, m. 169.5–70°.

Acetyl-*m*-oxybenzoate, $(C_2H_5O)O.C_6H_4.CO_2R$, m. 140°.

- p*-Toluate, $\text{CH}_3\text{C}_6\text{H}_4\text{CO}_2\text{R}$, m. 104.5° .
p-Thiol toluate, $\text{CH}_3\text{C}_6\text{H}_4\text{CO.S.R}$, m. 97° .
o-Creosotate, $\text{CH}_3\text{C}_6\text{H}_3(\text{OH})\text{CO}_2\text{R}$, m. 98.5° .
m-Creosotate, $\text{CH}_3\text{C}_6\text{H}_3(\text{OH})\text{CO}_2\text{R}$, m. 174° .
p-Creosotate, $\text{CH}_3\text{C}_6\text{H}_3(\text{OH})\text{CO}_2\text{R}$, m. 147° .
5-Iodosalicylate, $\text{I.C}_6\text{H}_3(\text{OH})\text{CO}_2\text{R}$, m. 141° .
5-Aminosalicylate, $\text{NH}_2\text{C}_6\text{H}_3(\text{OH})\text{CO}_2\text{R}$, m. 200.5° .
Acetylsalicylate, $\text{CH}_3\text{COO.C}_6\text{H}_4\text{CO}_2\text{R}$, m. 90.5° .
Anisate, *p*- $\text{CH}_3\text{O.C}_6\text{H}_4\text{CO}_2\text{R}$, m. 132° .
Vanillate, $\text{CH}_3\text{O.C}_6\text{H}_3(\text{OH}).\text{CO}_2\text{R}$, m. $140-1^\circ$.
Piperate, $\text{C}_{12}\text{H}_9\text{O}_4\text{R}$, m. 145° .
o-Nitrocinnamate, $\text{NO}_2\text{C}_6\text{H}_4\text{C}_2\text{H}_2\text{CO}_2\text{R}$, m. 132° .
m-Nitrocinnamate, $\text{NO}_2\text{C}_6\text{H}_4\text{C}_2\text{H}_2\text{CO}_2\text{R}$, m. 174° .
p-Nitrocinnamate, $\text{NO}_2\text{C}_6\text{H}_4\text{C}_2\text{H}_2\text{CO}_2\text{R}$, m. 186.5° .
Coumarate, $\text{C}_6\text{H}_4(\text{OH}).\text{C}_2\text{H}_2\text{CO}_2\text{R}$, m. 152.5° .
 β -Hydroxynaphthoate, $\text{C}_{10}\text{H}_6(\text{OH})\text{CO}_2\text{R}$, m. 164° .
Benzoic sulfinid ester, $\text{C}_6\text{H}_4\text{COSO}_2\text{N.R}$, m. 174.5° .
Isophthalate, $\text{C}_6\text{H}_4(\text{CO}_2\text{R})_3$, m. 202.5° .
Terephthalate, $\text{C}_6\text{H}_4(\text{CO}_2\text{R})_3$, m. 263.5° .
4,5-Dichlorophthalate, $\text{Cl}_2\text{C}_6\text{H}_2(\text{CO}_2\text{R})_2$, m. 164.5° .
Tetrachlorophthalate, $\text{Cl}_4\text{C}_6(\text{CO}_2\text{R})_2$, m. 180° .
3-Nitrophthalate, $\text{NO}_2\text{C}_6\text{H}_3(\text{CO}_2\text{R})_2$, m. 189.5° .
Mellitate, $\text{C}_6(\text{CO}_2\text{R})_6$ (?), m. $>300^\circ$.

BIOGRAPHY.

Edward Lyons was born in Botoken, Russia, in 1890. In 1900 he came to Baltimore, Maryland, where he attended public school. He was graduated from the Lexington High School, Lexington, Virginia, in 1909, and from Washington and Lee University (B.S.) in 1912. After another year at the University as a graduate student in chemistry he held the position of assistant in chemistry 1913-1914 and instructor 1914-1915. Following a brief stay in industrial work he entered the Johns Hopkins University in the fall of 1915.